

SOURCES AND GEOCHEMICAL EVOLUTION OF CYANIDE AND FORMALDEHYDE

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Although several systems have been proposed to be capable of molecular recognition and replication, only purine-pyrimidine base pairing has been experimentally demonstrated to perform those combined functions. Early precursors of RNA may be assumed to have utilized a minimum of two nitrogen bases attached to acyclic hydroxyaldehydes, and originally, or at a more advanced stage, to have incorporated phosphate linkages. Such an evolution would require satisfactory sources of cyanide, simple aldehydes, and reactive phosphate species. Furthermore, efficient geochemical mechanisms are needed to selectively concentrate these components into an environment where appropriate reactions can be demonstrated to be possible and probable.

The major source of cyanide has, in current paleoatmospheric models, been assumed to be the reaction of photodissociated thermospheric nitrogen with a limiting supply of stratospheric methane. Formaldehyde may be produced with more ease from an atmosphere with an atmosphere of carbon dioxide as the dominant carbon species, and from carbonate in solution or sorbed in double-layer hydroxide minerals.

Potentially more important sources for cyanide and other carbon containing molecules are the partially photoprotected northern and southern auroral ovals where continuous currents reaching several mega-amperes induce ion-molecule reactions, extending into the lower stratosphere - in simulated environments of this kind cyanide ion is known to be produced from oxidized carbon species potentially more abundant than methane.

Rainout of cyanide and formaldehyde place them in two different geochemical reaction reservoirs. In the anoxic Archean hydrosphere, about 1 mM in Fe^{2+} , cyanide ion would have been efficiently converted to the stable ferrocyanide complex $\text{Fe}(\text{CN})_6^{4-}$, protecting it from the commonly considered fate of decomposition by hydrolysis, and eventually incorporating it in pyroaurite materials type minerals, most efficiently in green rust where it converts to insoluble ferriferrocyanide, prussian blue.

In snow and firn the Sanchez-Orgel freezeout process would lead to eutectic concentration of glycolonitrile and its oligomers as reaction products of cyanide and formaldehyde, the latter probably always present in excess.

The cyanide in the hydrosphere, strongly bound to ferrous iron, is shown experimentally to be liberated on photooxidation of ferrocyanide with concurrent precipitation of $\gamma\text{-FeOOH}$. In the presence of an equimolar or larger fraction of formaldehyde in 10mM solution pH 7, the liberated cyanide practically completely converts to glycolonitrile.

The seemingly ubiquitous cyanohydrin production inferred from the Archean cryosphere and hydrosphere focuses the attention on the following evolution of these compounds. Glycolonitrile (formaldehyde cyanohydrin) in neutral or weakly alkaline solution oligomerizes along two different paths. One, kinetically favored at low temperatures, such as in the Sanchez-Orgel situation, leads to a crystallizable compound, presumed to be 6-amino-5-hydroxy-2,4-pyrimidine dimethanol. The prospect of spontaneous formation of such a pyrimidine from geochemically plausible source is of interest for biopoesis; the structure and reactivity of this model is now being investigated.

The second reaction of glycolonitrile, kinetically dominant at ambient temperature, produces a light yellow oligomer, which at increasing polymerization turns into a brown, viscous liquid and eventually to a black solid. Hydrolysis and pyrolysis of such a polymer may provide a source of amino compounds and ammonia, difficult to produce and maintain in the Archean atmosphere.